

## IV.B.1j Solutions for Chemical Hydrogen Storage: Dehydrogenation of B-N Bonds

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- (A) System Weight and Volume
- (B) System Cost
- (E) Charging/Discharging Rate
- (R) Regeneration Processes

### Technical Targets

Amineboranes are promising substances for chemical hydrogen storage, provided that efficient catalysts can be developed to liberate the stored hydrogen rapidly. This project is working to develop cost-effective catalysts for the dehydrogenation of amineboranes. We are also working to develop new mixed CBN materials that have the potential to be directly regenerated. Insights gained from these studies will be applied toward the design of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

Cost: \$4/kWh net  
Specific energy: 2 kWh/kg  
Energy density: 1.5 kWh/L

### Objectives

- Identify materials/systems to meet DOE target goals for gravimetric and volumetric densities of hydrogen. *Amineboranes and other boron-nitrogen (BN) compounds have potential for high hydrogen storage capacities.*
- Develop catalysts to meet DOE target goals for H<sub>2</sub> charging/discharging rates from BN materials. *Thermal hydrogen release from BN materials is slow and inefficient. Effective catalysts for dehydrogenation/hydrogenation will be needed.*
- Optimize system to obtain cost-effective catalysts. *Scale of project requires inexpensive and widely available components.*
- Optimize BN/carbon-boron-nitrogen (CBN) materials for potential in effective regeneration processes. *Efficient regeneration of spent BN materials is critical.*

### Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

### Accomplishments

- Used rational ligand design methods to significantly improve non-platinum group metal (PGM) catalyst activity and stability.
- Found that a tridentate pincer ligand motif is valuable in catalyst activity and stability.
- Experimentally measured the enthalpies of reaction for dehydrogenation of methylamine borane (MeAB) and 1:1 ammonia borane (AB)/MeAB mixtures.
- Demonstrated that dehydrogenation of the CBN material ethylenediamine bisborane (EDBB) occurs rapidly but only the B-N bonds (not the C-C bonds) are affected.
- Began synthetic development of new CBN materials with calculated enthalpies of dehydrogenation that are more favorable for direct regeneration (calculations in collaboration with University of Alabama).



### Introduction

In order for chemical hydrogen storage to be feasible the storage materials must have a high weight

percentage of hydrogen. Compounds containing carbon (C), boron (B) and nitrogen (N) are therefore promising. Furthermore, the discovery that dehydrogenation of B-N bonds is exothermic and the knowledge that dehydrogenation of C-C bonds is endothermic opens possibilities for tuning the thermodynamics of dehydrogenation by mixing carbon, boron and nitrogen in the same material. Another key aspect of this project is the rapid release of hydrogen from these materials through catalysis. We are working on developing and testing non-PGM catalysts for rapid dehydrogenation of B-N and C-C bonds.

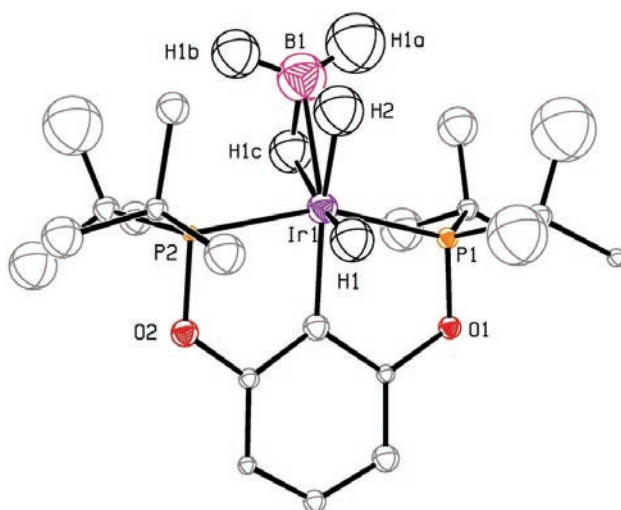
## Approach

Our approach to meeting the DOE targets is to rationally design non-PGM catalysts for the dehydrogenation of amine borane systems. Through ligand modification we are able to tune the catalyst for increased stability and activity. We are also concerned with the viability of direct regeneration of amine borane materials which affects whether the material might be suitable for on-board regeneration. We have directly measured the enthalpy of dehydrogenation for a variety of amine borane systems and determined that it will not be possible to regenerate them directly by reaction with hydrogen. Collaborations have been initiated with the University of Alabama to identify new mixed CBN materials which approach DOE targets and also have the potential for on-board regeneration. We are currently working on devising synthetic methods to prepare these novel materials.

## Results

The previously reported dormant form of the highly active Ir catalyst [1] has been fully characterized. A structure solved using neutron diffraction data shows that this complex contains a novel binding mode for a  $\text{BH}_3$  ligand in which a singular BH bond interacts with the metal center to form a  $\sigma$ -type complex (Figure 1). Several common borylation agents were reacted with the catalyst to further explore the ability of the Ir fragment to interact with a BH bond, including 9-borobicyclononane and pinacolborane. This work is in press in the *Journal of the American Chemical Society*.

As reported last year, the dehydrogenation of both MeAB and 1:1 mixtures of AB/MeAB using the Ir catalyst, (POCOP)IrH<sub>2</sub>, yields 1.0 equivalent of hydrogen and soluble BN products. The latter is important for engineering considerations of a fuel system within the automobile. Characterization of the MeAB soluble products by electrospray ionization mass spectrometry (ESI-MS) and gel permeation chromatography (GPC) is consistent with the formation of a mixture of oligomers. Similar results are observed for the 1:1 mixture of AB/



**FIGURE 1.** Structure Solved by Neutron Diffraction Data for the Dormant Ir Catalyst

MeAB, with the formation of co-oligomers observed by ESI-MS and GPC. Increasing the ratio of AB relative to MeAB resulted in formation of both soluble and insoluble products. The soluble products observed are identical to those observed in the 1:1 reactions; however the ratio of oligomers formed in the mixture is dependent on the starting ratio of AB relative to MeAB. Regardless of the initial AB/MeAB ratio, the soluble oligomeric products contain an approximate 1:1 ratio of dehydrogenated AB and MeAB units. The insoluble product is consistent with the previously reported cyclic pentamer  $[\text{NH}_2\text{BH}_2]_5$  [2].

In order to investigate the potential reversibility of these reactions, differential scanning calorimetry experiments were performed in collaboration with Tom Autrey and John Linehan at Pacific Northwest National Laboratory to determine reaction enthalpies. A reaction enthalpy of  $-6.8 \pm 0.6$  kcal/mol was determined for MeAB dehydrogenation, and a reaction enthalpy of  $-6.7 \pm 0.1$  kcal/mol was measured for the 1:1 AB/MeAB dehydrogenation. Both of these reaction enthalpies are similar to those measured for AB dehydrogenation, and suggest the reaction is too exothermic for direct regeneration of the spent fuel.

We have discovered a cobalt catalyst that rapidly dehydrogenates AB, giving one equivalent of hydrogen in 15 minutes at room temperature. The reaction was not poisoned by mercury, indicating that a homogeneous catalyst is involved in the dehydrogenation. Unfortunately this catalyst decomposes when the reaction is carried out at elevated temperature (60°C). The ligand structure was modified to produce a more stable cobalt catalyst; however the catalytic activity was greatly reduced. Examination of these prior systems allowed us to rationally develop a new cobalt catalyst with similar stability at 60°C and greatly increased

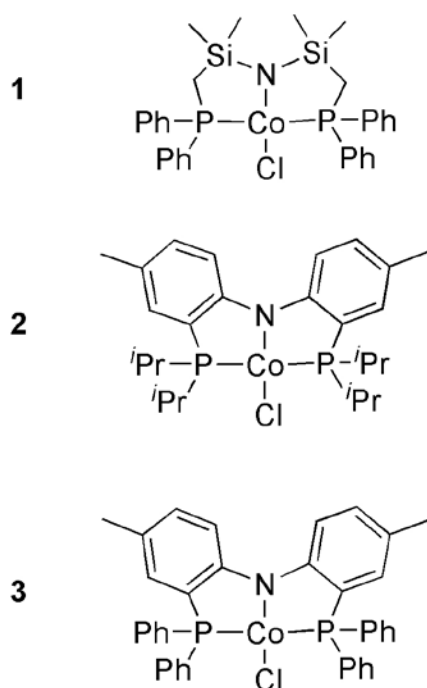


FIGURE 2. Cobalt Catalysts Used in Dehydrogenation Studies

TABLE 1. Summary of Cobalt Catalyst Performance

Catalyst	1	2	3
Equiv. H <sub>2</sub> Generated	One	One	One
Stability at 60 °C	Unstable	Stable	Stable
Induction Period	Variable	None	None
Reaction Time 22 °C	15 min	48 hrs	6 hrs
Reaction Time 60 °C	-	24 hrs	70 min

catalytic activity (Figure 2, Table 1). Further studies will focus on modifying this ligand system and other related ligands to optimize catalyst lifetime while increasing the dehydrogenation activity.

Direct measurements of the enthalpies of reactions have shown the thermodynamics of AB and MeAB dehydrogenation will be unfavorable for the direct regeneration of spent fuel. We are targeting new materials with potential for direct regeneration. Our efforts are focused on CBN materials that should yield more favorable thermodynamics by the coupling of the endothermic dehydrogenation of C-C bonds with the

exothermic dehydrogenation of B-N bonds. We have prepared and dehydrogenated the known CBN material EDBB. No C-C bond dehydrogenation was observed and only 2 equivalents of hydrogen were produced using the iridium catalyst noted above.

A cyclic CBN material may result in more facile dehydrogenation of C-C bonds. The CBN material, 1,2-azaboracyclohexane was targeted as a promising material. Calculations done by our collaborators at the University of Alabama indicated that dehydrogenation of this material to yield 3 equivalents of hydrogen would have a  $\Delta G_{\text{calc}} = -2.3$  kcal/mol at 298 K. The synthesis of this material is in progress.

## Conclusions and Future Directions

While the iridium catalyst is very efficient at dehydrogenating a variety of amine borane systems its high cost makes it unfeasible for this application. However, insight gained from studying this system has allowed us to prepare three new cobalt catalysts that have been shown to be active in dehydrogenation of amine boranes. Further modification of these systems will likely improve their overall performance. Mixed CBN materials are also being pursued for their potential for direct regeneration. Calculations have suggested 1,2-azaboracyclohexane may fit the requirements and this material is currently being synthesized. Further studies on CBN materials will be dependent on finding catalysts that can dehydrogenate both B-N and C-C bonds.

## FY 2008 Publications/Presentations

- Sigma Borane Complexes of Iridium: Synthesis and Structural Characterization.* Travis J. Hebden, Melanie Denney, Vincent Pons, Paula Picolli, Arthur J. Schultz, Tom Koetzle, Werner Kaminsky K. I. Goldberg, and D. M. Heinekey, *J. Am. Chem. Soc.* 2008, in press.
- A Convenient One Pot Synthesis of di(*t*-butyl)phosphinic chloride.* Daniel F. Brayton, Karen I. Goldberg, Werner Kaminsky and D. M. Heinekey. *Phosphorus, Sulfur, and Silicon and the Related Elements*, in press.
- Iridium Catalyzed Dehydrogenation of Substituted Amine-Boranes: Kinetics, Thermodynamics and Implications for Hydrogen Storage.* Brandon L. Dietrich, Karen I. Goldberg, D. M. Heinekey, Tom Autrey, John Linehan, submitted to *Inorganic Chemistry*.
- Coordination Chemistry of Dihydrogen: Structure, Dynamics and Reactivity.* D. M. Heinekey. Presented at the Organometallic Chemistry Gordon Conference, Newport, RI, July 2007.
- Catalysts for Hydrogen Release from Amine Borane Compounds.* D. M. Heinekey. Presented at Argonne National Laboratory User's Meeting, May 2007.

6. *New Catalysts for Dehydrogenation of Amine Boranes*. D. M. Heinekey, Denise Méry, Melanie C. Denny, Karen I. Goldberg, Brandon L. Dietrich, Nathan A. Bennette, Travis Hebden. Presented at the 234<sup>th</sup> ACS National Meeting, Boston, MA, August 2007.
7. *Catalysts for Hydrogen Release from Amine Borane Compounds*. D. M. Heinekey. Presented at the second LANL-NEDO-AIST Workshop on Fuel Cell Performance Improvement and Hydrogen Storage Materials, Tokyo, October 2007.
8. *Solutions for Chemical Hydrogen Storage: Dehydrogenation of B-N Bonds*. Brandon Dietrich, Tony St. John, Travis Hebden, Nathan Bennette, Dan Brayton, D. M. Heinekey, Karen I. Goldberg. Presented at the DOE Hydrogen Program Annual Review Washington D.C., June 2008.

## References

1. Denny, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048.
2. Bøddeker, K. W.; Shore, S. G.; Bunting, R. K. *J. Am. Chem. Soc.* **1966**, *88*, 4396.